

Appendix B

Recalculation of ferric iron in amphibole

Amphibole recalculation follows a method similar to that of Spear and Kimball (1984) and Robinson et al. (1982), extended as follows: To ensure a reasonably stoichiometric amphibole, we suggest eight crystal-chemical constraints which may be applied, in addition to the constraints of all ferrous or all ferric iron. For an amphibole microprobe analysis recalculated on the basis of 23 oxygens with a cation sum Σ , we argue that too little ferric iron has been allocated if:

1. $\Sigma > 16$ (too many cations for an amphibole)
2. $\text{Si} > 8$ (too much silicon)
3. $(\Sigma - \text{Na} + \text{K}) > 15$ (all sodium has been forced from M4-into the A-site)
4. $\text{Ca} > 2$ (some calcium has been forced out of the M4-site)
5. All iron as ferrous (minimum possible)

Too much ferric iron has been allocated if:

6. $(\text{Si} + \text{total Al}) < 8$ (there are not enough tetrahedral cations)
7. $(\Sigma - \text{K}) < 15$ (all Na has been forced from the A-site onto the M4-site)
8. $(\Sigma - \text{Na} - \text{K} - \text{Ca}) < 12.9$ (too many vacancies on the M1, M2, M3 and T sites)
9. $\text{Fe}^{3+} > (2 - \text{Al}^{\text{vi}} - \text{Ti})$ (ferric iron can only go on the M2-sites)
10. All iron as ferric (maximum possible)

N.B. Constraint 8 is usually made in terms of $\Sigma - \text{Na} - \text{K} - \text{Ca} = 13$ cations; we have relaxed this to 12.9 because, although the calcic amphiboles in Deer et al. (1963) and Robinson et al. (1982) do cluster about 13.0, they may range down to below 12.9 cations. As our method relies on this constraint as an upper limit on ferric iron, we prefer this slightly wider constraint.

The method suggested here begins by recalculating the microprobe analysis on the basis of 23 oxygens assuming all Fe as FeO. Increasing the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio has the effect of decreasing the cation sum and the problem reduces to finding a factor f which can be used to renormalise (reduce) the cation totals to satisfy each of the constraints noted above.

Proceed by first calculating values for all the f_i according to the criteria noted above:

group A (upper bound on f)	group B (lower bound on f)
$f_1 = 16/\Sigma$	$f_6 = 8/(\text{Si} + \text{Al}_{\text{total}})$
$f_2 = 8/\text{Si}$	$f_7 = 15/(\Sigma - \text{K})$
$f_3 = 15/(\Sigma - \text{Na} - \text{K})$	$f_8 = 12.9/(\Sigma - \text{Na} - \text{K} - \text{Ca})$
$f_4 = 2/\text{Ca}$	$f_9 = 36/(46 - \text{Al}_{\text{total}} - \text{Si} - \text{Ti})$
$f_5 = 1.00$	$f_{10} = 46/(\text{Fe}_{\text{tot}} + 46)$

If any f value from group A is larger than 1.00 it offers no constraint and should be set to 1.00, i.e. taking all iron as Fe^{2+} . If any f from group B is larger than 1.00 then the amphibole cannot be made stoichiometric. Choose the smallest value (f_A) from group A and the largest value (f_B) from group B. We seek an average value f_{av} which is bracketted by f_A and f_B (with f_A larger than f_B). If f_B is larger than f_A then the analysis fails one of the above criteria for stoichiometry. With the f_{av} so obtained, renormalise all the cations (which have so far been determined assuming all Fe as FeO) by multiplying each cation $i(C_i)$ by the factor f_{av} , such that $C_i \rightarrow f_{av} C_i$ and the cation total goes to $f_{av} \Sigma$. Then the amounts of ferric and ferrous iron are given by $\text{Fe}^{3+} = 46(1 - f_{av})$ and $\text{Fe}^{2+} = \text{Fe}_{\text{total}} - \text{Fe}^{3+}$. The factor 46 comes from the 23 oxygens basis on which the charge balance recalculation is made.

Site allocations

From the final recalculated analysis first determine cm, the "cummingtonite" substitution:

$$\text{cm} = \text{Si} + \text{Al} + \text{Ti} + \text{Fe}^{3+} + \text{Fe}^{2+} + \text{Mg} + \text{Mn} - 13.0$$

Then the required site terms for the thermometers may be found as follows:

$$\begin{aligned} X_{\text{Si}}^{\text{T1}} &= (\text{Si} - 4)/4 \\ X_{\text{Al}}^{\text{T1}} &= (8 - \text{Si})/4 \\ X_{\text{Al}}^{\text{M2}} &= (\text{Al} + \text{Si} - 8)/2 \\ X_{\text{K}}^{\text{A}} &= \text{K} \\ X_{\square}^{\text{A}} &= 3 - \text{Ca} - \text{Na} - \text{K} - \text{cm} \\ X_{\text{Na}}^{\text{A}} &= \text{Ca} + \text{Na} + \text{cm} - 2 \\ X_{\text{Na}}^{\text{M4}} &= (2 - \text{Ca} - \text{cm})/2 \\ X_{\text{Ca}}^{\text{M4}} &= \text{Ca}/2 \end{aligned}$$

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